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(54) TEXTILE TREATING COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a Company organised under the laws of the State of Ohio, United States of America, of 301, East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The invention relates to compositions and a method for treating fabrics in an aqueous bath such as the final rinse after a washing process to improve various properties of the fabric.

It has been known for several years that fabrics can be made to feel softer by treatment in a dilute solution or dispersion of certain cationic quaternary ammonium derivatives, and rinse-additive compositions have been marketed for this purpose.

The present invention surprisingly makes it possible to provide substantial additional benefits by an unexpected combination of fabric conditioning agents. These benefits may include some or all of: easier ironing, anti-static properties, pleasanter feel of the fabrics, soil release properties. It appears that recognition of improved "ease of ironing" can arise from a combination of at least three factors, namely fewer wrinkles to be removed, wrinkles more easily removed (e.g. with less weight upon the iron), or more completely removed, and less effort required to slide the iron along the fabric. "Pleasanter" feel can be consistently observed by experienced judges, although it is not easy to define in words the sensation or combination of sensations they like. Anti-static and soil release properties improve the achieving and maintaining of soil-free fabrics.

The combination of agents of the invention involves the presence of both a cationic compound having one or more long chain alkyl groups and a silicone, as further defined hereinbelow.

Silicones have been used to provide various benefits, for instance as water-proofing agents and as "ironing aids", but have usually been applied to the fabrics, during manufacture or during make-up of articles of clothing, in the form of relatively concentrated dispersions or solutions of silicones, either by processes such as padding, or by spray on. In other words, the prior art treatments have relied upon treatment with relatively concentrated, e.g. 2—3% by weight and upwards, dispersions or solutions of silicones to ensure that some silicone remained upon the surface of the fabrics. Often, especially for water-proofing treatment, the fabric was subsequently treated with catalysts to cause cross linking or setting of the silicone. If normal commercial silicones are applied to fabrics from dilute aqueous systems, they are not substantive

to a useful degree, that is insufficient silicone is present in the dilute residual liquor in the fabric to provide any appreciable effect, and therefore the advantageous effects of the silicone on the fabrics are greatly reduced or lost.

It has now surprisingly been found that if a silicone is incorporated, even at very low concentrations, in a bath containing certain fabric substantive cationic textile softeners, the silicone and softener being used in certain proportions, the silicone, together with the textile softener, tends to migrate to the surface of the fabric and becomes substantive, and concentrated thereon. Thus, there can be achieved a very desirable overall effect involving both softening benefits and such additional benefits as mentioned hereinabove. These latter can be varied by varying the silicone.

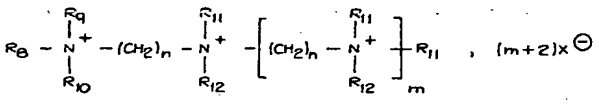
According to the present invention there is provided a textile treating composition in the form of an aqueous dispersion comprising:

(a) a fabric substantive cationic compound selected from

(i) quaternary mono-ammonium compounds having either two C_{12}—C_{20} alkyl chains or one C_{18}—C_{24} alkyl chain;

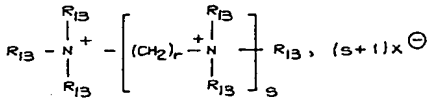
(ii) quaternary imidazolinium textile softeners;

(iii) polyammonium compounds of the general formula



wherein R_8 is a straight or branched chain C_{10}—C_{22} alkyl group or alkenyl group; R_{10}, R_{11} and R_{12} are independently selected from hydrogen, C_1—C_3 alkyl, $(C_2H_4O)_pH$ or $(C_3H_6O)_qH$, wherein $p+q$ is $\leqslant 25$; R_9 is defined as R_8 or as R_{10}, R_{11} and R_{12}; m is from 0 to 8, n is from 2 to 6 and $X^{\ominus}$ is an anion;

(iv) compounds of the general formula:



wherein R_{13} is hydrogen or a C_1—C_4 alkyl group, r is an integer from 2 to 6, s is not less than 3 and $X^{\ominus}$ is an anion; and

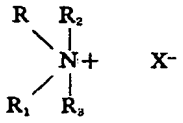
(v) mixtures thereof; and

(b) an emulsion of a predominantly linear di(C_1—C_3) alkyl or alkyl-aryl siloxane in which the alkyl groups may be partially or wholly fluorinated and which may be substituted with cationic nitrogen groups, the siloxane having a viscosity at 25°C of at least 100 centistokes and up to 8000 centistokes; the weight ratio of the siloxane content of component (b) to component (a) being in the range from 5:1 to 1:100.

The weight ratio of the siloxane content of component (b) to component (a) preferably lies in the range from 2:1 to 1:10, especially from 1:1 to 1:3.

Fabric substantive cationic component

The cationic compounds suitable include those commonly used in rinse-added textile softening compositions. They include quaternary ammonium salts of general formula



wherein either (a) R_2 and R_3 (which may be the same or different) represent methyl, ethyl, propyl or benzyl, and either R and R_1 each represent a straight or branched chain alkyl group having 12 to 20 carbon atoms, or R represents a straight or branched chain alkyl group having 18 to 24 carbon atoms and R_1 represents methyl, ethyl, propyl or benzyl; or (b) R_2 and R_3 together with the nitrogen atom form a 5-membered or 6-membered heterocyclic ring and R represents a straight or branched

chain alkyl group having 18 to 24 carbon atoms; and X^- is an anion. The long chain alkyl groups may be derived from natural fats e.g. coconut, or more preferably tallow, or from petroleum or synthetically.

In a preferred group of salts of formula (I), R and R_1 each represent an alkyl group having 16 to 18 carbon atoms, R_2 and R_3 each represent methyl, and X^- represents Cl^-, Br^- or $OSO_3CH_3^-$.

Other anions include nitrite, acetate and phosphate.

Specific examples of particularly preferred cationic softening agents include the following:

—tallowtrimethyl ammonium chloride,
—tallowdimethyl (3-tallowalkoxypropyl) ammonium chloride,
—ditallow dimethyl ammonium chloride,
—ditallow dimethyl ammonium methyl sulphate,
—eiicosyltrimethyl ammonium chloride, and
—dieicosyldimethyl ammonium chloride.

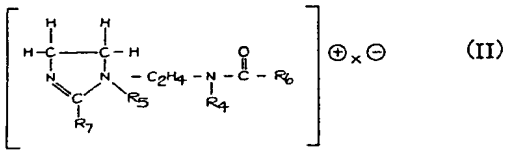
Examples of other suitable cationic softening agents suitable for use in the invention herein include the following:

—ditetradecyldimethyl ammonium chloride,
—dipentadecyldimethyl ammonium chloride,
—didodecyldiethyl ammonium chloride,
—didodecyldipropyl ammonium chloride,
—ditetradecyldiethyl ammonium chloride,
—ditetradecyldipropyl ammonium chloride,
—ditallowdiethyl ammonium chloride,
—ditallow dipropyl ammonium chloride,
—tallowdimethyl benzyl ammonium chloride,
—tallowdiethyl benzyl ammonium chloride,
—didodecyldiethyl ammonium acetate,
—tallowtrimethyl ammonium acetate,
—tallowdimethyl benzyl ammonium nitrite, and
—ditallowdipropyl ammonium phosphate.

Other cationic softening agents of formula (1) are known and include variations wherein R and R_1 can also represent a phenyl radical or a hydroxy-substituted alkyl of 1, 2 or 3 carbon atoms.

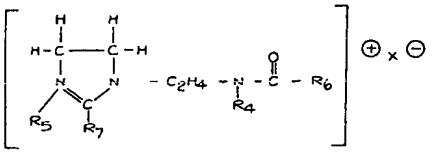
Many other cationic quaternary ammonium softening agents, which are useful herein, are known; for example, alkyl [C_{12} to C_{20}]-pyridinium chlorides, alkyl [C_{12} to C_{20}]-alkyl [C_1 to C_3]-morpholinium chlorides, and quaternary derivatives of amino acids and amino esters.

Cationic quaternary imidazolinium compounds are also suitable as softening agents in the compositions herein. The structure of these compounds is not fully established but is believed to be either



(II)

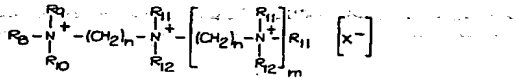
or



wherein R_4 represents hydrogen or alkyl having 8 to 25, preferably at least 15, carbon atoms, R_5 represents alkyl having 1 to 4, preferably 1 or 2, carbon atoms, R_6 represents alkyl having 1 to 4 carbon atoms or hydrogen, R_7 represents alkyl having 8 to 25, preferably at least 15, carbon atoms and X^- is an anion, preferably methyl sulphate or chloride. Other suitable anions include bromide, acetate, nitrite and phosphate.

Particularly preferred are those compounds of formula (II) in which both R_4 and R_7 represent alkyl having 16 to 25 (especially 16 to 18 or 20 to 22) carbon atoms.

A further group of fabric substantive cationic compounds suitable for use in the present invention is characterised by the following general formula



(III)

wherein R_8 is a straight or branched chain C_{10}—C_{22} alkyl group or alkenyl group, R_{10}, R_{11} and R_{12} are independently selected from hydrogen, C_1—C_3 alkyl, $(C_2H_4O)_pH$ and $(C_3H_6O)_qH$ wherein $p+q$ is $\leqslant 25$ and wherein not all of the R_{10}, R_{11} and R_{12} groups are C_1—C_3 alkyl, R_9 is defined as R_8 or as R_{10}, R_{11} and R_{12}, m is from 0 to 8, n is from 2 to 6 and $X^{(-)}$ represents one or more anions having a total charge balancing that of the nitrogen atoms. (Highly preferred compounds of this group are the acid salts of diamine compounds where m=o in formula (III) above). Particularly preferred compounds within this group are N-C_{16-18} alkyl N,N,N^1,N^1,N^1, pentamethyl-1,3-propane diamine diacetate and dichloride (i.e. where $R_8=C_{16}$—C_{18} alkyl R_9 R_{10} R_{11} $R_{12}=CH_3$ m=o X=Cl or CH_3COO— in III above).

Another preferred class of compounds within the above group are the fabric softening polyamine salts, i.e. those compounds of formula (III) above in which at least one of the groups on each nitrogen atom is a hydrogen atom. N—C_{16}—C_{18} alkyl N,N^1N^1 triethanol-1,3-propane diamine dichloride or diacetate (i.e. where $R_8=C_{16}$—C_{18} alkyl R_9 R_{11}-C_2H_4OH R_{10} and R_{12}=hydrogen m=o and x=Cl^- or CH_3COO^- in III above) is an example of this class.

Acid salts of diamine compounds, as used herein, are the addition products formed when certain acids add to the amino moieties of the diamines and form mono- or di-ammonium salts.

The diamine acid salts can be partially acidified diamine salts (i.e. only one nitrogen atom quaternized with acid) of fully acidified diamine salts (i.e. both nitrogen atoms quaternized with acid).

A variety of acids can be used herein to form the acid salts so long as the anion of the diamine acid salt formed is stable under fabric rinse conditions and is non-interfering in the rinse. Suitable acids include organic and inorganic acids such as hydrochloric acid, =acetic acid, sulphuric acid, lactic acid, stearic acid, formic acid, citric acid and a large variety of others. Particularly preferred acids used to form diamine acid salts include acetic acid and hydrochloric acid.

Nonlimiting examples of such diamine acid salts include:

$[C_{16}H_{33}—NH(CH_3)—(CH_2)_3—NH(CH_3)_2]^{++}$ $(CH_3COO)_2^-$

$[C_{18}H_{37}—NH(CH_3)—(CH_2)_2—NH(C_2H_5)_2]^{++}$ $(CH_3COO)_2^-$

$[C_{12}H_{25}—NH(CH_3)—(CH_2)_3—H_2N—C_{12}H_{25}]^{++}$ Cl_2^-

$[C_{12}H_{25}—NH(C_2H_5)—(CH_2)_3—NH(C_3H_7)_2]^{++}$ $(CH_3SO_4)_2^-$

$[R_{Tallow}$ $NH_2—(CH_2)_3—NH(C_2H_5)_2]^{++}$ Br_2

$[C_{20}H_{41}—NH(CH_3)—(CH_2)_2—NH(CH_3)_2]^{++}$ Cl_2

$[C_{15}H_{31}—NH(C_2H_5)—(CH_2)_3—NH_3]^{++}$ $(CH_3COO)_2$

$[C_{18}H_{37}—NH_2—(CH_2)_3—H_2N—CH_3]^{++}$ $(HCOO)_2^-$

$[C_{16}H_{33}—NH_2—(CH_2)_3—H_2N—C_{16}H_{33}]^{++}$ Cl_2^-

$[R_{Tallow}$ $NH(CH_3)—(CH_2)_3—NH(C_2H_5)_2]^{++}$ $(CH_3COO)_2^-$

$[C_{16}H_{33}NH(CH_3)—(CH_2)_3—NH(C_2H_5)_2]^{++}$ $(CH_3SO_4)_2^-$

$[C_{12}H_{25}NH(C_2H_5)—(CH_2)_2—NH(C_3H_7)_2]^{++}$ Cl_2^- and

$[C_{14}H_{29}NH(CH_3)—(CH_2)_3—(CH_3)NH—(C_8H_{17})]^{++}$ $(CH_3COO)_2^-$

wherein in the above formulae R_{Tallow} is the alkyl group derived from tallow fatty acid.

Other examples of suitable compounds include those in which the starting diamine is N-tetradecyl, N'-propyl-1,3-propane-diamine; N-eicosyl,N,N',N'-triethyl-1,2-ethane-diamine and N-octadecyl, N,N',N'-tripropyl-1,3-propane-diamine.

The form in which the diamine acid salt is derived is not critical. The diamine acid salt can be formed from diamines *in situ* during the preparation of the aqueous fabric conditioning compositions herein or can alternatively, for example, be obtained as the acid salt from commercial sources (e.g. Duomac T marketed by Armour-Hess Co). Mixtures of diamine acid salts can, of course, be used as the static control agent in the compositions of the present invention.

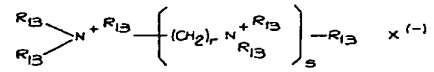
The fully acidified diamine salts (i.e. the diacid salts) are particularly preferred inasmuch as these materials permit formation of highly stable, clear, aqueous liquid fabric conditioning compositions.

Preferred aqueous fabric conditioning compositions contain diamine acid salts wherein R_1 is alkyl of from about 16 to about 18 carbon atoms; and R_2, R_3 and R_4 are hydrogen or alkyl of from about 1 to about 2 carbon atoms and n is 2 or 3, more preferably 3.

Diamine acid salts useful in the invention herein are commercially available under a variety of trade marks including Duomeens and Duomacs (marketed by Armour-Hess Co) and Dinozem and Dinoremac (marketed by CECA/Pierrefitte-Auby). Moreover, the starting diamine compounds can be prepared in accordance with processes disclosed in the art, as, for example, in U.S. Patent 2,267,205 issued December 23, 1941 to Kyrides and U.S. Patent 2,246,524 issued June 24, 1941 to Kyrides.

Also within the scope of the polymeric compounds embraced by formula (III) are fully substituted, i.e. quaternised compounds. As indicated above, these polyquaternary compounds do not consist wholly of C_1—C_3 alkyl substituent groups but also contain a level of polyalkenoxy substitution which may be polyethenoxy, polypropenoxy or mixtures of the two and in which each poly alkenoxy chain consists of not more than 25 units.

Polyalkylene imine salts have also been found to be of value in the present invention. These salts have the general formula:



(IV)

wherein R_{13} is hydrogen or a C_1—C_4 alkyl group, r is an integer from 2—6, preferably from 2—4 and most preferably 2, s is not less than 3, preferably from 6—24 and X is as defined above. Preferably R_{13} is methyl and s has a value from 8 to 16.

Silicone Component

As mentioned previously, the silicone component is an aqueous emulsion of a predominantly linear polydialkyl or alkyl, aryl siloxane in which the alkyl groups can have from one to five carbon atoms and may be wholly or partially fluorinated. Suitable silicones are polydimethyl siloxanes having a viscosity at 25°C in the range from 100 to 8,000 centistokes preferably in the range from 1000 to 5000 centistokes.

As recited hereinbefore, the combination of a fabric substantive quaternary ammonium textile softening compound and a silicone of the above type materially improves the substantivity of the latter. It is postulated that this enhanced substantivity arises from a 'carrier' effect by means of which the positivity charged fabric softener molecules associate with the silicone molecules and cause them to migrate to the fabric surface. However, experiments have shown that the distribution of this combination on the fabric is less than optimum i.e. some areas of fabric receive a high concentration of silicone while others receive very little if any silicone.

It has however been found that the ionic charge characteristics of the silicone as used in the combination are important in determining both the extent of deposition and the evenness of distribution of the silicone and hence the properties of a fabric treated therewith.

Silicones having cationic character show an enhanced tendency to deposit.

As mentioned above, silicones found to be of value in providing fabric feel benefits have a predominantly linear character and are preferably polydialkyl siloxanes in which the alkyl group is most commonly methyl. Such silicone polymers are frequently manufactured commercially by emulsion polymerisation using a strong acid or strong alkali catalyst in the presence of a nonionic or mixed nonionic-anionic emulsifier system.

In combination with the cationic fabric softening agent, anionic- or nonionic emulsified silicone polymers tend to aggregate in dilute aqueous solution due to the attraction between the negatively or non-charged emulsifier and the positively charged fabric softening agent. However, the provision of a silicone emulsion having a like charge to that of the fabric softening agent would tend to reduce this effect and a further reduction might be expected from the tendency of the charged silicone-droplets to repel each other.

Thus, in the present invention, the silicone component embraces a silicone of cationic character which is defined as being one of

(a) a predominantly linear di C_1—C_5 alkyl or C_1—C_5 alkyl, aryl siloxane, prepared by emulsion polymerisation using a cationic surfactant as emulsifier.

(b) an α,ω-di quaternised di C_1—C_5 alkyl or C_1—C_5 alkyl, aryl siloxane polymer or

(c) an amino-functional di C_1—C_5 alkyl or alkyl aryl siloxane polymer in which the amino group may be substituted and may be quaternised and in which the degree of substitution (d.s.) lies in the range 0.001 to 0.1, preferably .01—0.075.

provided that the viscosity at 25°C of the silicone is from 100 to 8,000 cs.

a) Cationic emulsion polymerised siloxanes

Cationic emulsion polymerised siloxanes are known in the art and can be prepared by strong alkali or acid catalysis of siloxane monomer(s) in the presence of a cationic emulsifying agent. Hyde and Wehryl U.S. Patent No. 2,891,920 describes general procedures for such polymerisations and Examples 1—6 of the patent provide specific teaching of the required reaction conditions. The siloxane monomer can be any di lower alkyl siloxane such as dimethyl, diethyl dipropyl, or ethyl butyl siloxane or alkyl, aryl siloxane such as methyl, phenyl siloxane or ethyl phenyl siloxane. However, the preferred starting material for emulsion polymerisation is normally a cyclic trimer or tetramer of the desired siloxane.

The emulsifying agent can be any one of a wide range of cationic surfactants such as:

Aliphatic fatty amines and their derivatives such as dodecylamine acetate, octadecylamine acetate and acetates of the amines of tallow fatty acids; homologues of aromatic amines having fatty chains such as dodecylaniline; heterocylic aliphatic diamine derivatives such as undecylimidazoline; fatty amines derived from disubstituted amines such as oleylaminodiethylamine; derivatives of ethylene diamine; quaternary ammonium compounds such as dioctadecyldimethyl ammonium chloride, didodecyldimethyl ammonium chloride and dihexadecyldimethyl ammonium chloride; amide derivatives of amino alcohols such as β-hydroxyethylstearyl-amide; amine salts of long chain fatty acids; quaternary ammonium bases derived from fatty amides of di-substituted diamines such as oleylbenzylaminoethylene diethylamine hydrochloride; quaternary ammonium bases of the benzimidazolines such as methylheptadecyl benzimidazol hydrobromide; basic compounds of pyridinium and its derivatives such as cetylpyridinium chloride; sulfonium compounds such as octadecylsulfonium methyl sulfate; quaternary ammonium compounds of betaine such as betaine compounds of diethylamino acetic acid and octadecylchloromethyl ether; the condensation products of stearic acid and diethylene triamine; polyethylene diamines; and polypropanol-polyethanol amines.

The emulsifier is conventionally employed at a level of 1%—10% by weight of the siloxane, more preferably 0.5%—5% by weight.

The catalyst employed to polymerise the siloxane is preferably an alkaline catalyst such as an alkali metal hydroxide or a quaternary ammonium hydroxide of the formula $(R°)_4N^+OH^-$. In such ammonium hydroxides the R° groups can be hydrogen or alkyl radicals such as methyl, ethyl, propyl, butyl, isobutyl, decyl or octadecyl or aralkyl radicals such as benzyl or hydroxyalkyl radicals such as hydroxyethyl, hydroxypropyl and hydroxybutyl.

Most preferably the catalyst is a quaternary ammonium hydroxide having at least one radical of at least 12 carbon atoms in chain length, such a material also serving as an emulsification agent. Long chain length alkyl quaternary ammonium salts are also preferred as the emulsification agents, particularly di-long chain alkyl di-lower alkyl quaternaries, such as ditallowyl dimethyl ammonium chloride (DTDMAC), available commercially from Armour Chemical Company as Arquad 2HT (Arquad is a Registered Trade Mark) and imidazolinium derivatives such as methyl C_{18} alkyl amidoethyl, C_{18} alkyl imidazolinium methosulphate, available commercially from Ashland Chemical Company as Varisoft 475 (Varisoft is a Registered Trade Mark).

The level of catalyst usage is dependent on the catalyst type employed. Acid catalysts are conventionally used at high levels, e.g. at 15% or more by weight of the aqueous phase of the emulsion. Alkaline catalysts by contrast are used at lower levels, e.g. from 0.001% to 10%, preferably from 0.1% to 5% by weight of the siloxane monomer.

Emulsion polymerisation of dimethyl siloxane using DTDMAC as emulsifier

In a typical preparation, dichloro dimethyl siloxane was first hydrolysed to form octamethyl cyclo tetra siloxane using the method of Patnode and Wilcock in JACS *68* 1946 pp 358—363. 15 grs of this material were then added to a mixture of 131 grs of a 1% aqueous solution of ditallowyl dimethyl ammonium chloride and 3.75 grs of tetrabutyl ammonium hydroxide in the form of a 40% aqueous solution. The mixture was stirred during addition of the ingredients by means of a Silverson (trade mark) laboratory emulsifier mixer and, after addition was complete, the reaction mixture was subjected to 15 minutes further agitation using an ultrasonic vibrator. After 18 hours at 80°C the emulsion was neutralised and the poly dimethyl siloxane oil was precipitated from the reaction mixture by addition of 500 mls of ethyl alcohol and was then dried with further alcohol before being heated at 75°C under a high vacuum to remove all volatile materials. The viscosity of the silicone was determined to be 22,000 centistokes by measurement of its rate of flow under gravity between two marks on a calibrated tube. The time taken for a given quantity to flow along the tube was converted to viscosity using a calibration curve established with commercial silicones of known viscosity.

Using the above-described polymerisation technique, stable 10% emulsions of polydimethyl siloxane were achieved and equivalent results were obtained when the procedure was repeated using cetyl trimethyl ammonium bromide and the imidazoline derivative Varisoft 475 respectively as the emulsifier.

b) α-ω quaternised polysiloxanes

The preparation of α,ω quaternised siloxane polymers can be conveniently carried out using the method disclosed in I.C.I. British Patent Specification No. 1,006,729. In this technique a polysiloxane end-stopped with alkyl halide groups in which the halogen atoms are separated from the nearest silicon atoms by at least three carbon atoms, is reacted with a tertiary amine to give an α,ω-quaternised siloxane polymer. In order to provide the polysiloxane starting material a solution polymerisation is normally carried out to give a polymer of the appropriate molecular weight, and the polymerisation reaction is terminated by reaction with a ω-halo alkyl dimethyl silanol.

As previously stated, the polysiloxane can be a poly di (C_1—C_5 alkyl)- or (C_1—C_5 alkyl, aryl) siloxane, preferably a polydimethyl siloxane and the tertiary amine can be any alkyl, aryl or mixed alkyl and aryl material. Examples include trimethylamine, cetyl dimethyl-amine, pyridine, phenyl dimethyl-amine.

Preparation of a α-ω dipyridinium polydimethyl siloxane

A typical preparation of this class of silicone polymers involved the polymerisation of 23.2 grs of octamethyl cyclotetra siloxane in the presence of 0.9 mls of concentrated sulphuric acid and 2.5 grs of 1,3-bis, 3-chloropropyl tetramethyl disiloxane. The mixture was shaken in a sealed flask for 48 hours at room temperature, following which 5 mls of water were added and the flask shaken for a further hour. The resulting emulsion was split by addition of 50 mls of diethyl ether and the organic layer was then washed twice with 30 ml aliquots of distilled water, dried over sodium bicarbonate and magnesium sulphate and filtered. Evaporation of the filtrate to remove the ether left 23 grs of a clear oil of viscosity 100 cs. NMR examination of the oil showed it to correspond to a polymer having 36 siloxane units.

10 grs. of the α,ω-bis(3 chloropropyl) silicone prepared above were then refluxed in 10 mls pyridine for 36 hours at 120°C. Excess pyridine was distilled off under reduced pressure leaving a brown viscous oil. This was then dissolved in toluene, washed with water and the toluene layer dried and evaporated to remove the toluene. NMR spectral analysis disclosed a level of proton activity corresponding to 70—80% of the theoretical uptake of pyridine.

10% aqueous emulsions of the silicone product were prepared by mechanical emulsification using an ethoxylated linear alcohol emulsifying agent (Dobanol* 45E4, a C_{14}—C_{15} linear alcohol tetra ethoxylate supplied by Shell International Chemicals Limited) at a level of 20% by weight of the siloxane.

* Dobanol is a Registered Trade Mark.

c) Amino functional linear polysiloxanes

Amino functional linear polysiloxanes can be prepared by the general method disclosed in British Patent Specification No. 1,339,906 at page 3 lines 78—108, page 4 lines 1—65 and page 3 lines 3—14. In this method, a hydrosiloxane is reacted with an alkenyl group-containing tertiary amine in the presence of a platinum catalyst in accordance with the equation

$$(Me_3SiO)_2\ (SiMe_2O)_x(SiMeHO)_y + yCH_2{=}CHR'NR_2 \xrightarrow{H_2PtCl_6} (Me_3SiO)_2\ (SiMe_2O)_x(OSi(Me)R''NR_2)_y$$

wherein x=10 to 100, y=1 to 20, R is a methyl, ethyl or phenyl group, R′ is a direct linkage or a divalent organic group free of aliphatic unsaturation containing 1—16 carbon atoms and R″ is a divalent organic group free of aliphatic unsaturation containing 2—18 carbon atoms.

The product of the above reaction can then be quaternised by further reaction with an alkyl halide or can be converted to the hydrochloride by acidification with hydrochloric acid.

Preparation of polydimethyl siloxane substituted with dimethylaminopropyl groups

In a typical preparation 50 grs of dimethyl-methyl hydrogen siloxane copolymer containing approximately 76 dimethyl siloxane units and 6 hydromethyl siloxane units was dissolved in 50 mls toluene containing a trace of chlorplatinic acid. The mixture was stirred under nitrogen at 80°C, 5.18 grs of N,N-dimethyl allylamine in 10 mls of toluene was added dropwise, holding the reaction temperature at 80—90°C., and the reaction mixture was stirred for a further 2 hours and then cooled. Sodium carbonate was added to neutralise any remaining acid and the mixture was filtered and rotary evaporated to remove solvents, leaving a pale yellow fluid of low viscosity. NMR analysis showed the formation of poly dimethyl siloxane containing dimethylaminopropyl groups at a level corresponding to a reaction completeness of 80%+, and a degree of substitution (d.s.) of 0.06.

20 grs of the reaction product was stirred in 100 mls of a 1:1 mixture of dichloromethane and isopropanol and 1.3 mls of concentrated HCl (11.21M) in 10 mls of the same solvent mixture was added slowly at room temperature. Following evaporation of the solvent a pale coloured solid was left and NMR analysis showed this material as having a proton ratio close to the expected value for the hydrochloride derivative with no detectable level of the starting material. The siloxane polymer was then made up into a 10% aqueous emulsion using 20% based on the siloxane weight of a nonionic emulsification agent (Dobanol* 45E4, a linear C_{14}—C_{15} alcohol containing 4 moles of ethylene oxide supplied by Shell International Chemicals Limited).

A similar experimental technique to the above was employed to produce polydimethyl siloxanes having respectively approximately 40 siloxane units and a d.s. of 0.04 and 72 siloxane units with a d.s. of 0.015.

The concentration of the aqueous dispersions (by which term is included solutions) which constitute the compositions of the invention is not critical and is controlled by practical considerations. Accordingly, the dispersions should be concentrated enough not to be wasteful in transit costs, yet should be sufficiently aqueous to maintain the silicone component in emulsified form and fluid enough to disperse readily in a usage bath. Usually a content of from about 1% to 20%, especially about 3—10% by weight of components (a) and (b) together is convenient. Thus, the compositions can take the form of an aqueous dispersion or solution of comparatively low viscosity (i.e. 200 centistokes or below) or of a paste, cream or gel. As stated earlier, the ratio of the siloxane portion of component (b) to the quaternary softening agent of component (a) should be in the ratio of from 5:1 to 1:100, preferably from 2:1 to 1:10 and most preferably from 1:1 to 1:3.

Optional Components

The aqueous dispersions may contain other components, such as nonionic emulsifying aids, which are used at levels of the order of 1% by weight of the composition to aid dispersion of the usually poorly soluble cationic softeners. A wide range of nonionic emulsifiers can be used for this purpose such as those disclosed in German Patent Application OLS 2500111 published July 17th, 1975. It has also been

* Dobanol is a Registered Trade Mark.

found that use of emulsifiers is sometimes desirable to aid the dispersion of the silicones in the compositions of the invention, especially when silicones of relatively high viscosity are employed.

Highly preferred optional ingredients also include nonionic fabric treatment agents such as the fatty acid partial esters of mono- or polyhydric alcohols or anhydrides thereof having from 1 to about 8 carbon atoms in the alcohol. In these compounds the fatty acid ester should have at least 1, more preferably at least 2, fatty acyl groups. The alcohol portion of the ester can be ethylene glycol, glycerol, diglycerol, xylitol, sucrose, erythritol, pentaerythritol, sorbitol or sorbitan; sorbitan esters are particularly preferred.

The fatty acid portion of the ester normally comprises a fatty acid having from 12 to 22 carbon atoms, typical examples being lauric acid, myristic acid, palmitic acid, stearic acid and behenic acid.

Amongst these esters, the most preferred are the glyceryl esters of stearic acid, especially glyceryl monostearate, and the sorbitan fatty acid esters, which are esterified dehydration products of sorbitol. Nonionic fabric conditioning materials of this type are commonly employed at levels of 1—10% preferably 2—4% by weight of the composition.

Other preferred ingredients include pyrodextrins such as British Gum and White dextrin and substituted dextrins such as dextrin phosphates, cationic dextrins and dextrin pyrollidone carboxylic acid, in which the degree of substitution is from 0.01 to 2.0 preferably 0.05 to 1.5. A preferred cationic dextrin is a white dextrin that has been reacted with glycidyl trimethyl ammonium chloride to provide a degree of substitution (d.s.) in the dextrin molecule of from about 0.1 to 1.0. The dextrins are used at levels of 0.5% to 5% by weight of the compositions, preferably at levels of 1% to 3%.

Non-aqueous, water miscible solvents may be present, and other viscosity controlling agents, such as low levels of electrolytes. Other optional components include appropriate optical brighteners, fungicides and germicides, colouring or opacifying agents, and perfumes.

Preferred compositions embodying the invention contain by weight of the composition 2—4% of a ditallowyl dimethyl ammonium salt, 1—2% of a linear polydimethyl siloxane prepared by emulsion polymerisation in the presence of a cationic emulsifying agent and 1—2% of a cationic pyrodextrin such as a white dextrin modified with glycidyl trimethyl ammonium chloride to give a d.s. of 0.8—0.9. Other exemplary compositions comprise 3—6% of a N-stearyl N-methyl N'dimethyl 1—3 propane diamine salt or its fully quaternised derivative, 1—2% of a polydimethyl siloxane of viscosity 100—3000 centistokes, polymerised with a nonionic-anionic emulsifier system and 2—5% of glyceryl monostearate. Optional additional components include 1—3% of an unmodified white dextrin and 2—4% of a quaternary ammonium softening agent such as DTDMAC.

In use the compositions of the invention are normally incorporated in an aqueous bath containing the ingredients of the compositions in the ratios defined hereinabove, at a concentration such that there is present from about 20 to 1,000 parts per million by weight of components (a) and (b) together of which at least 10 ppm is component (b). Preferably the bath contains from about 50 to 200 ppm of components (a) and (b) together of which at least 15 and up to 150 ppm is component (b).

The invention also embraces a method of treating textiles and textiles when so treated, which method comprises steeping them in such a bath.

The textiles may be steeped in such a bath and then dried on any occasion, but it is envisaged that normally the treatment will constitute the final rinse after a washing process.

Various non-limitative compositions are described below to exemplify the invention and were evaluated using the following test procedures:

Product Application

Clean test pieces of cotton or other fabric were treated in a domestic washing machine. Either a whole standard load was made up of test pieces or additional clean fabrics were used to make up the load. The machine cycle was set so that the load was subjected to gentle agitation (as for a wool wash cycle) for about 20 minutes in a solution of the test product in water, and was then spin-dried.

Wrinkling test

Treated test pieces were compared with a standard set of 8 plastic simulated test pieces of different degrees of wrinkling (American Association of Textile Chemists and Colourists—Three dimensional durable press replicas for use with AATCC Test 124).

Number 8 graded perfect, Number 1 worst. A grade 5—7 was deemed to represent about that degree of freedom from wrinkling at which a housewife might be expected to consider ironing unnecessary.

Ease of Ironing test

This was judged by a panel of judges, employing a Scheffe analysis to provide gradings (panel score units -psu) and a "yardstick", i.e. least difference significant at 95% probability.

End Result Test

A visual preference, graded as above in psu.

Softness test

A tactile preference, graded as above in psu.

Drying of Fabrics

The "spin-dried" test pieces were dried by hanging in the laboratory (static drying) or in a tumbler dryer.

Example I

Comparison of silicones having different viscosities

The effect of silicone viscosity on the wrinkle grade, ease-of-ironing grade and ironed-end-result grade of cotton tea towels treated with compositions of the invention was examined for a range of polydimethyl siloxanes prepared by emulsion polymerisation using a cationic emulsifier.

Seven aqueous compositions [of which (A)—(D) were for comparison purposes, (E)—(G) being according to this invention] were made up, each containing 6% DTDMAC and 3% of a silicone emulsion polymerised in the presence of 1% DTDMAC on a silicone basis. The siloxane polymers varied in viscosity from 1000 to 170,000 centistokes. The compositions were applied at 0.2% concentration to the fabrics simulating a final rinse treatment in a conventional washing cycle and the treated fabrics were then air dried and graded by a panel of judges. In such panel testing a difference between fabrics of approximately 0.5 panel score units (psu) in wrinkle grade is normally detectable by the housewife, while for ease of ironing and ironing end result a panel score unit difference of between 0.75—1.0 between fabrics is generally necessary in order for a difference to be noticeable.

The results are shown below, indexed to the grades obtained with a cationic-emulsified silicone of viscosity 170,000 centistokes.

	Siloxane Viscosity cs	Wrinkle Grade	Ease of Ironing	Ironed end result
(A)	170,000	0	0	0
(B)	100,000	+0.2	0	+0.5
(C)	40,000	+0.3	+0.1	−0.2
(D)	20,000	+0.4	+0.8	+1.2
(E)	8,000	+0.6	+0.7	+1.7
(F)	3,700	+0.6	+1.1	+2.1
(G)	1,000	+0.5	+0.8	+1.3

It can be seen that performance for these parameters improves with a reduction in viscosity from 170,000 cs, with the optimum appearing to lie in the range 3,000—8,000 cs.

EXAMPLE II

Five compositions (A)—(E) in accordance with the invention were made up and tested for ease of ironing, wrinkle grade, ironed end result and softness, using a commercially available fabric softening product containing 5.8% ditallowyl dimethyl ammonium chloride as the standard. Positive figures denote an advantage for the test product and vice versa. An asterisk denotes a significant difference at the 95% level of confidence.

Formulation	Levels (A)	(B)	(C)	(D)	(E)
N-tallowyl, N-methyl-N'dimethyl-1,3-propane diamine hydroacetate	4	4	4		
N-tallowyl, N-methyl N'dimethyl-1,3-propane diamine hydrochloride				4	4
Glyceryl monostearate	2	2	2	2.5	4.5
Releasil 8 (a nonionic emulsified polydimethyl siloxane of viscosity 1000 cs) available from Dow Corning ("Releasil" is a trade mark)	2	2	2	2	1.5[3]
Unmodified White Dextrin			3.0[1]		
Cationic pyro dextrin		2.9[2]			
Ease of ironing	+0.78*	+ .82*	+1.2*	1.2*	+0.92*
Wrinkling	+0.32*	+0.04	−0.3*	+0.28	+0.02
Ironed end result		−0.10	−0.26*	+0.3*	+0.22*
Softness	+0.3			+0.56*	+1.24*

1. White dextrin supplied by Remy, Belgium.
2. Reaction product of glycidyl triethyl ammonium chloride with white dextrin to give a d.s. of 0.85.
3. Q2-1070—A nonionic emulsified polydimethyl siloxane of viscosity 350 cs available from Dow Corning.

It can be seen that the compositions of the invention provide an improvement in ease of ironing and, with one exception, an improvement in wrinkle grade of the fabrics prior to ironing, and in ironed end result. Softness of the treated fabric was also enhanced in those instances where this variable was measured.

EXAMPLE III

A fabric treating composition (A) in accordance with this invention was made up comprising, by weight,

3 part DTDMAC
15 „ 10% Aqueous emulsion of Polydimethyl siloxane of viscosity 5000 centistokes prepared by emulsion polymerisation in the presence of 10% DTDMAC emulsifier (based on siloxane weight).
1.50 „ cationic pyrodextrin comprising British Gum modified by reaction with glycidyl trimethyl ammonium chloride to give a d.s. of 0.07.
0.50 „ nonionic emulsifier (50:50 mixture of Tergitol (trade mark) 15S3 and 15S9 secondary-alcohol ethoxylates marketed by Union Carbide)
0.35 „ colour perfume and miscellaneous
79.65 „ water.

This composition was compared with a commercially available aqueous fabric softener (B) containing 6% DTDMAC for ease of ironing, ironed end-result, anti-wrinkling (i.e. appearance before ironing), softness and feel/body, on cotton and polyester-cotton blend pillowcases, linen-cotton tea towels and terrycotton towels.

Each product was applied in the final rinse of an automatic 60°C. wash cycle in 21°H water, followed by spin drying and static drying indoors.

Test results are given below. Ease of ironing, ironed end result and softness are reported in panel score units with the poorer result expressed as zero. Anti-wrinkling results are reported as absolute grades.

	Cotton Pillowcases			Polycotton Pillowcases			Teatowels		
	B	A	lsd	B	A	lsd	B	A	lsd
Ease of Ironing	0.00	1.80	0.24	0.00	1.60	0.73	0.00	0.20	0.94
	0.00	1.10	0.69	0.00	1.30	0.61	0.00	0.40	0.66
Ironed End Result	0.00	0.72	0.90	0.00	0.00	0.69	0.24	0.00	0.94
	0.04	0.00	0.75	0.26	0.00	0.80	0.42	0.00	1.08
Anti-wrinkling	1.85	1.90		3.30	3.85		2.70	2.75	
	1.25	1.35		3.50	3.35		1.35	1.40	
				Terry Towels					
Softness				0.14	0.00	0.30			
				0.00	0.26	0.49			

Feel/body was expressed in terms of preference of a 20-member panel.

	Test I			Test II		
	B	A	No preference	B	A	No preference
Cotton pillowcases	6	11	3	6	12	2
Poly/cotton	7	8	4	9	9	2
Tea Towels	6	12	2	1	16	3
Terry Towels	7	10	3	5	12	3

It can be seen that composition A, in accordance with the invention, provides significantly better Ease of Ironing and Body/Feel benefits, as well as an overall advantage in Appearance before Ironing (Anti-wrinkling) and equivalent Ironed End Result performance.

WHAT WE CLAIM IS:—

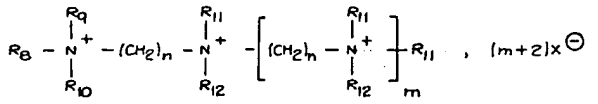
1. A textile treating composition in the form of an aqueous dispersion comprising:

(a) a fabric substantive cationic compound selected from

(i) quaternary mono-ammonium compounds having either two C_{12}—C_{20} alkyl chains or one C_{18}—C_{24} alkyl chain;

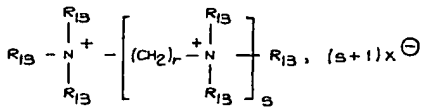
(ii) quaternary imidazolinium textile softeners;

(iii) polyammonium compounds of the general formula



wherein R_8 is a straight or branched chain C_{10}—C_{22} alkyl group or alkenyl group; R_{10}, R_{11} and C_{12} are independently selected from hydrogen, C_1—C_3 alkyl, $(C_2H_4O)_pH$ or $(C_3H_6O)_qH$, wherein $p+q$ is $\leqslant 25$; R_9 is defined as R_8 or as R_{10}, R_{11} and R_{12}; m is from 0 to 8, n is from 2 to 6 and $X^{\ominus}$ is an anion;

(iv) compounds of the general formula:



wherein R_{13} is hydrogen or a C_1—C_4 alkyl group, r is an integer from 2 to 6, s is not less than 3 and $X^{\ominus}$ is an anion; and

(v) mixture thereof; and

(b) an emulsion of a predominantly linear di(C_1—C_3) alkyl or S_1—C_5 alkylaryl siloxane in which the alkyl groups may be partially or wholly fluorinated and which may be substituted with cationic nitrogen groups, the siloxane having a viscosity at 25°C of at least 100 centistokes and up to 8000 centistokes;

the weight ratio of the siloxane content of component (b) to component (a) being in the range from 5:1 to 1:100.

2. A composition according to claim 1 wherein the quaternary monoammonium compounds has the formula

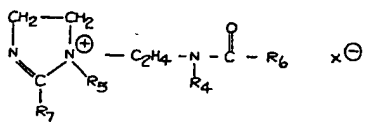
$$R\ R_1\ R_2\ R_3\ N^{\oplus}\ X^{\ominus}$$

wherein X is an anion and either

(i) R and R_1 each represent a straight or branched chain C_{12}—C_{20} alkyl group and R_2 and R_3 are independently selected from C_1—C_3 alkyl and benzyl groups or R_2 and R_3, together with the nitrogen atom, form a 5- or 6-membered heterocyclic ring; or

(ii) R represents a straight or branched chain C_{18}—C_{24} alkyl group, R_1 represents a C_1—C_3 alkyl or benzyl group and R_2 and R_3 are as hereinabove defined.

3. A composition according to claim 1 wherein the quaternary imidazolinium softener has the general formula



wherein R_4 is hydrogen or a C_1—C_4 alkyl group, R_5 is a C_1—C_4 alkyl group, R_6 is a C_8—C_{25} alkyl group, R_7 is a C_8—C_{25} straight or branched chain alkyl group and $X^{\ominus}$ is an anion.

4. A composition according to Claim 3 wherein the weight ratio of the siloxane content of component (b) to component (a) is from 2:1 to 1:10.

5. A composition according to any one of the preceding claims in which component (b) comprises a linear poly di(C_1—C_3 alkyl) siloxane prepared by emulsion polymerisation using a cationic emulsifier.

6. A composition according to claim 5 wherein the cationic emulsifier is a fabric softening cationic surfactant.

7. A composition according to any one of claims 1—4 wherein component (b) is an α,ω-diquaternised linear di(C_1—C_3 alkyl) siloxane polymer.

8. A composition according to claim 7 wherein the quaternising group comprises an aromatic molecule.

9. A composition according to any one of claims 1—4 wherein component (b) comprises a linear di(C_1—C_3 alkyl) siloxane polymer in which from 0.001% to 0.1% of the siloxane units contain an amino substituent group.

10. A composition according to claim 9 in which the degree of substitution (d.s.) lies in the range from 0.01% to 0.075%.

11. A composition according to any one of claims 1—4 wherein the component (b) is a polydimethylsiloxane.

12. A composition according to Claim 11 wherein the polydimethyl siloxane has a viscosity at 25°C of 1,000—5,000 centistokes.

13. A composition according to any one of the preceding claims containing from 1%—20% by weight of components (a) and (b).

14. A fabric treating composition according to claim 13 containing from 3% to 10% by weight of components (a) and (b).

15. A fabric treating composition substantially as described with reference to any one of the Examples I (E)—(G), Examples II (A)—(E) and Example III (A).

16. A method of treating fabrics comprising the step of steeping them in an aqueous bath containing a composition as claimed in any one of claims 1—15 said bath containing from 20—1000 parts per million (ppm) by weight of components (a) and (b) together of which at least 10 ppm is component (b).

17. Fabrics when treated by the method according to claim 16.

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